TITLE: COMBINED THEORETICAL AND EXPERIMENTAL INVESTIGATION OF MECHANISMS AND KINETICS OF VAPOR-PHASE MERCURY UPTAKE BY CARBONACEOUS SURFACES

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ABSTRACT

OBJECTIVE
The overall goal of this research program is to gain fundamental understanding of the important chemistry and physics involved in mercury adsorption on carbonaceous surfaces. This knowledge will then be used to optimize adsorption processes and operating conditions to maximize the uptake of mercury within the required contact time. An additional long-term benefit of this research is the basic understanding of the Hg adsorption process, which may facilitate the design of new adsorbents for more efficient and cost-effective removal of Hg from a variety of effluent streams. Molecular modeling of the adsorption of Hg on carbonaceous surfaces will greatly increase the insight into the physics of the adsorption process and combined with in situ rate measurements of mercury adsorption and desorption (conventional and pulsed laser) on graphite using linear and nonlinear optical probes with real time optical resolution have the potential to provide fundamental insight into the process of mercury uptake by carbonaceous surfaces. Besides accurate assessment of key parameters influencing adsorption equilibrium, fundamental understanding of the kinetics of mercury adsorption, desorption, and diffusion will be developed in this study. These key physical and chemical processes postulated through molecular modeling efforts and verified by in situ measurements will be utilized to select (or develop) promising sorbents for mercury control, which will be tested under dynamic conditions using simulated flue gas.

ACCOMPLISHMENTS TO DATE
- We have successfully completed the design and construction of a vacuum chamber that will be used to study mercury adsorption on graphite. Sample mount provides for both heating and cooling in vacuum and the optical access to the sample is possible over a range of angles (normal to grazing incidence).
- We have also designed and constructed a gas mixing/dosing system using a 6-way gas-mixing chamber connected downstream of a vacuum chamber incorporating a leak valve.
- The optical arrangement to be used to measure adsorption induced reflectivity changes was setup and baseline test performed to determine the original noise level of the optical system

including laser source. The optical signal is reported in terms of normalized change in reflectivity. The baseline drift was 0.3% over a long-term (30 min) and 0.1% over short-term (1 min).

- We have carried out a thorough review of the literature on the interaction between mercury (Hg) and graphite, and also Hg-Hg interactions. This highlighted certain key features that should be included in *ab initio* calculations involving Hg. In general, there is essentially no *ab initio* work on the Hg-graphite system.
- A single Hg atom lying above the center of a benzene ring was used as a preliminary model system to study the Hg-graphite interaction.
- We decided to use an effective core potential (ECP), which includes both relativistic effects and spin-orbit coupling, in our calculations on Hg and benzene with Gaussian98. These calculations are to allow us to assess the type of interaction, the binding energy and the electron-density distribution between Hg and benzene, and the validity of density functional theory, specifically the Becke3 and LYP exchange and correlation functionals. The main basis set superposition error contribution is thought to come from the *5s5p5d* core, therefore it is important to adopt an ECP, such as this one, which includes all 20 of these electrons in the valence shell rather than just the 12 electrons in the *5d* and *6s* orbitals. In order to optimize the basis set we have calculated the polarizability, ground state, and excited state energies of the Hg atom. There is good agreement with the available experimental data. However, the dimer binding energy is not well reproduced---it is approximately 10% of the experimental value. Even MP2 gives us a value of half the measured value. Therefore, it seems that DFT will not be suitable for representing the Hg-Hg fluid interaction.
- We have identified a number of Hg-Hg pair potentials in the literature. These potentials will be evaluated through molecular simulations.

PLANS FOR THE COMING YEAR

- Assembly and testing of vacuum chamber and gas mixing dosing system.
- Design and construction of temperature controller for sample
- Adsorption experiments using differential reflectivity initially at room temperature
- Isothermal and temperature programmed desorption experiments
- We will code various Hg-Hg potentials from the literature and perform molecular simulations to assess the accuracy of the potentials by comparing with experimental data such as the gas and liquid phase equation of state, the second virial coefficient, and perhaps transport properties.
- We will run Gaussian98 calculations on Hg with benzene, napthalene and larger cluster models for graphite at both the MP2 and B3LYP levels of theory, and using the optimized Hg basis sets. We will be able to assess how well B3LYP can represent the Hg/graphite interaction by comparing the potential energy surface mapped out by these different methods.
- Identify the most favorable adsorption sites and the type of adsorption which occurs from the Hg-benzene, Hg-napthalene, etc. calculations.
- Develop more accurate models for the graphite sheet and assess the convergence of the interaction potential.

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